

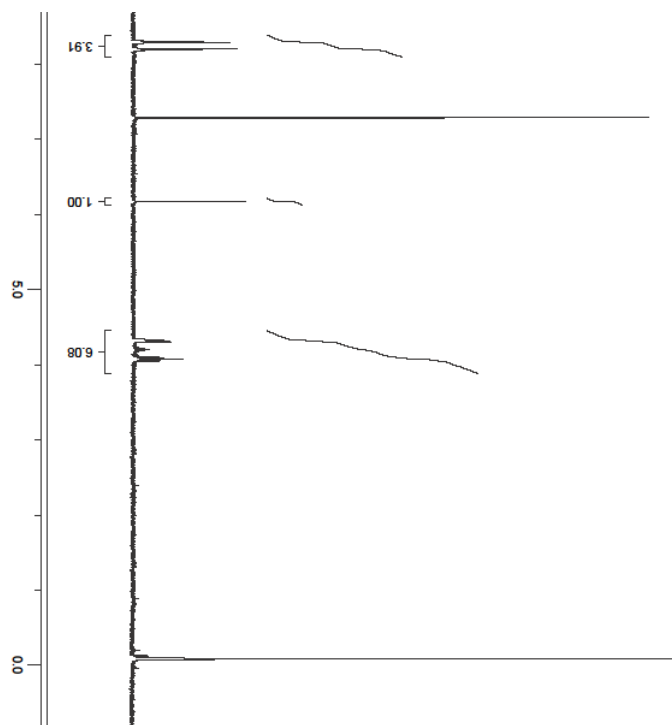
Influence of nanoscale phase separation on geminate versus bimolecular recombination in P3HT:fullerene blend films.

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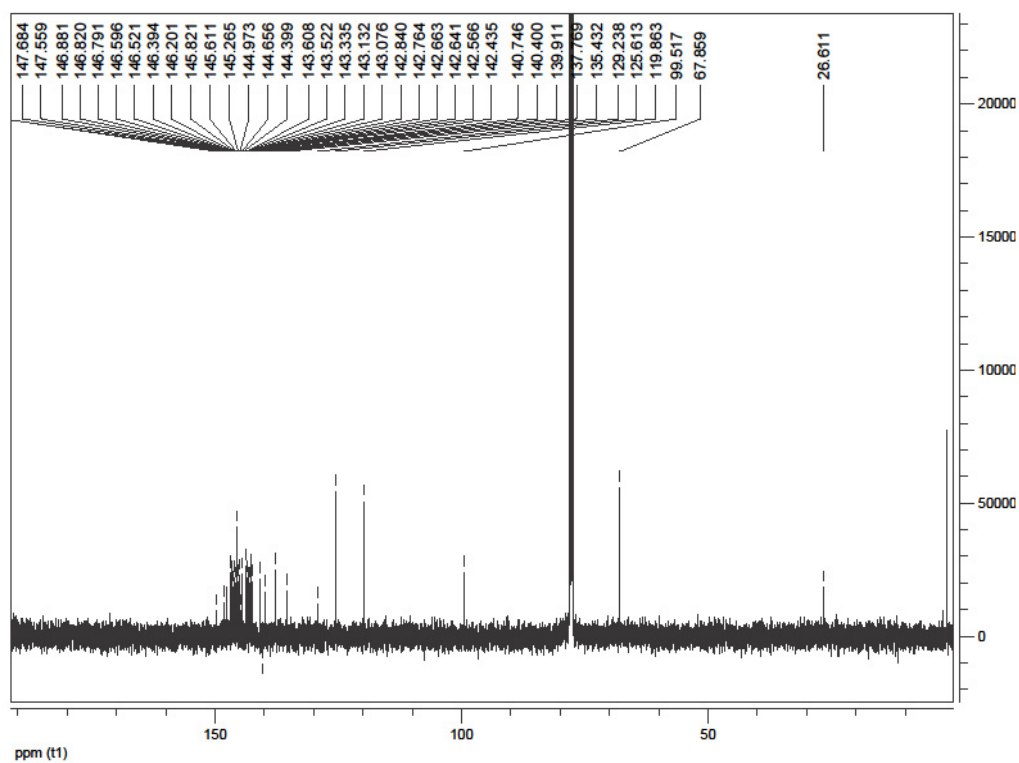
Supplementary Information

Yield of C₆₀-2

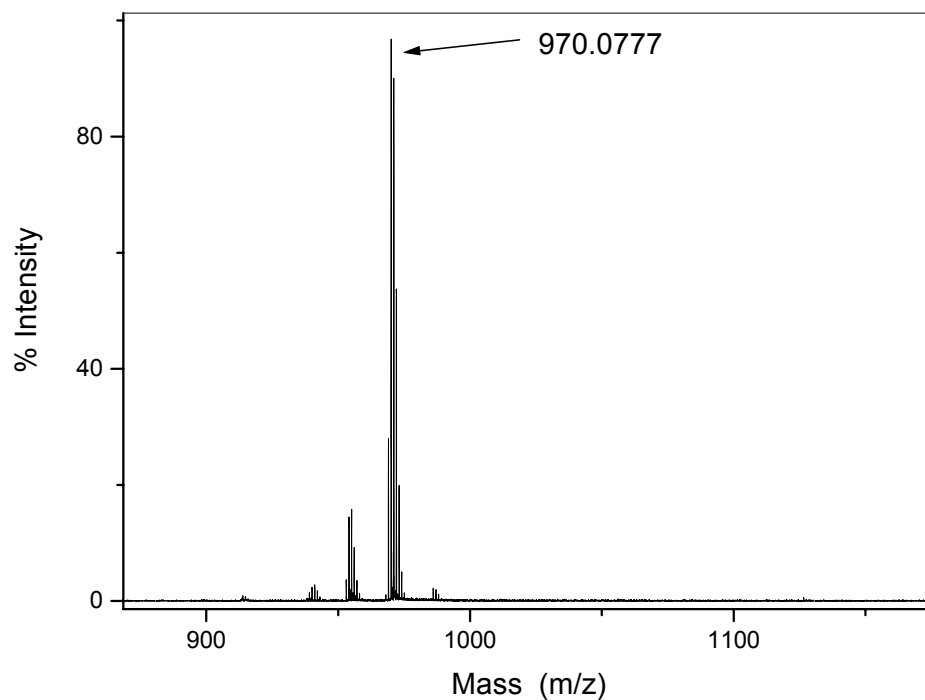
Yield: 127 mg were obtained 80%. ¹H NMR (CDCl₃/CS₂) δ 8.27 (d, *J*=9.2 Hz, 2H), 8.17 (d, *J*=9.2 Hz, 2H), 6.14 (s, 1H), 4.0-4.3 (m, 6H). ¹³C NMR (CDCl₃/CS₂) δ 149.65, 148.04, 147.68, 147.55, 146.88, 146.82, 146.79, 146.59, 146.52, 146.39, 146.20, 145.82, 145.61, 145.26, 144.97, 144.65, 144.39, 143.60, 143.52, 143.33, 143.13, 143.07, 142.84, 142.76, 142.66, 142.64, 142.56, 142.43, 140.74, 140.40, 139.91, 137.76, 135.43, 129.23, 125.61, 119.86, 99.51, 67.85, 26.61. FT-IR (KBr): 2922, 1591, 1508, 1324, 527 cm⁻¹. UV-vis (Toluene) λ 284, 332, 428. MS *m/z* 970.07 (M+1). Calculated for C₇₁H₁₁N₃O₄: 969.07.



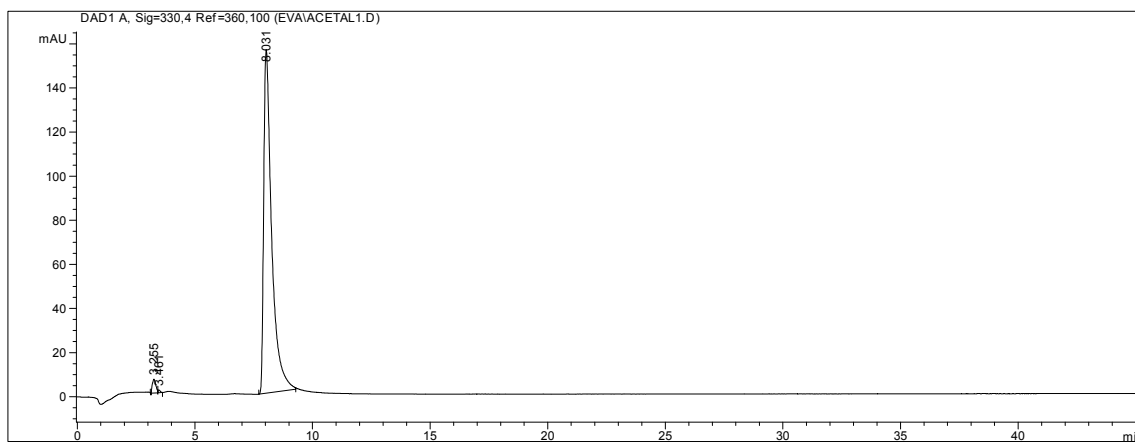
$^1\text{H-NMR}$ of **2** $\text{CDCl}_3/\text{CS}_2$



$^{13}\text{C-NMR}$ of $\text{C}_{60}\text{-2}$ $\text{CDCl}_3/\text{CS}_2$



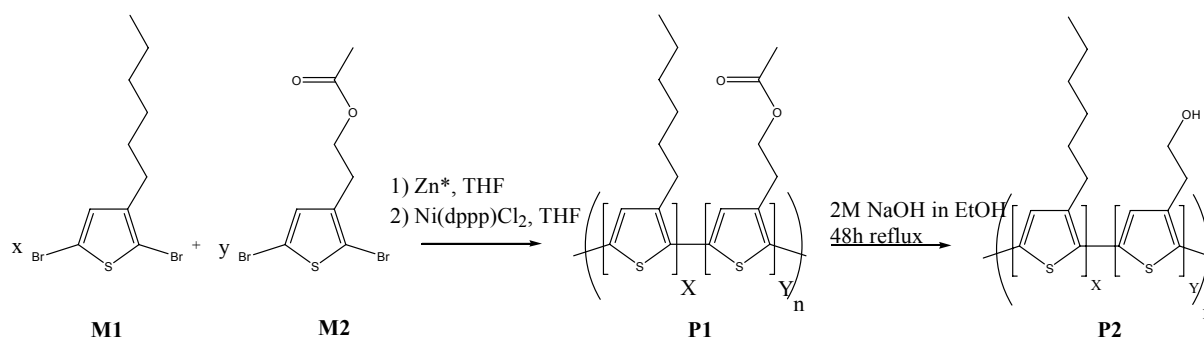
Mass Spectroscopy of C₆₀-2



HPLC of C₆₀-2 Toluene 1mL/min.

Synthesis of poly([3-hexylthiophene-2,5-diyl]-co-[3-(2-acetoxyethyl)thiophene-2,5-diyl]) (P1, P3HT) and poly([3-hexylthiophene-2,5-diyl]-co-[3-(2-hydroxyethyl)thiophene-2,5-diyl]) (P2, P3HT-OH):

The molecular structure of P3HT has been adapted by means of copolymerization using the *Rieke* method for production of regioregular polymers^[1] and post-polymerization functionalization reactions^[2] (Scheme 1).^[1]The monomers 2,5-dibromo-3-hexylthiophene (M1) and 2,5-dibromo-3-(2-acetoxyethyl)thiophene (M2) have been synthesized following literature procedures.^[3, 4] The *Rieke* method allowed for the synthesis of functionalized regioregular poly(3-alkylthiophene)s (RR P3AT)s by copolymerization, since it tolerates functional groups in the side chain because of the selective oxidative addition of zinc to the aromatic halide.^[5] Using a bulk copolymerization procedure, the regio-regular ester-functionalized copolymer P1, containing 10% of ester functions has been synthesized. The percentage of ester-functionalized side chains in copolymer P1 proved to be the same as the percentage of M2 in the mixture of monomers M1 and M2, as determined by ¹H-NMR. The ester functions in P1 were then hydrolyzed towards the alcohol functions and copolymer P2 was isolated. The conversion of the ester groups in P1 to alcohols in P2 is followed through the disappearance of the CH₃ singlet at $\delta=2.06$ ppm in ¹H-NMR and of the C=O absorption around 1740 cm⁻¹ on FT-IR.



Scheme S1. Rieke copolymerization of M1 and M2 in a (9/1) ratio, with post-polymerization hydrolysis.

Polymer	R [a]	x/y [b]	Yield [%] [d]	RR [%] [e]	M _w [f]	M _n	D
P3HT		1/0	67	96	33 900	19 000	1.8
P1	-(CH ₂) ₂ - OC(O)CH ₃	9/1	61	94	47 700	24 700	1.9
P2	-(CH ₂) ₂ -OH	9/1	98	93	68 100	31 100	2.2

[a] functionalized polymer side chain, [b] molar ratio of repeating units in monomer feed [c] molar ratio of repeating units in the copolymer, determined with ¹H-NMR [d] yield after purification [e] percentage of head-tail couplings determined on ¹H-NMR [f] M_w, M_n and D are weight average, number average and polydispersity in THF.

Steady state absorption

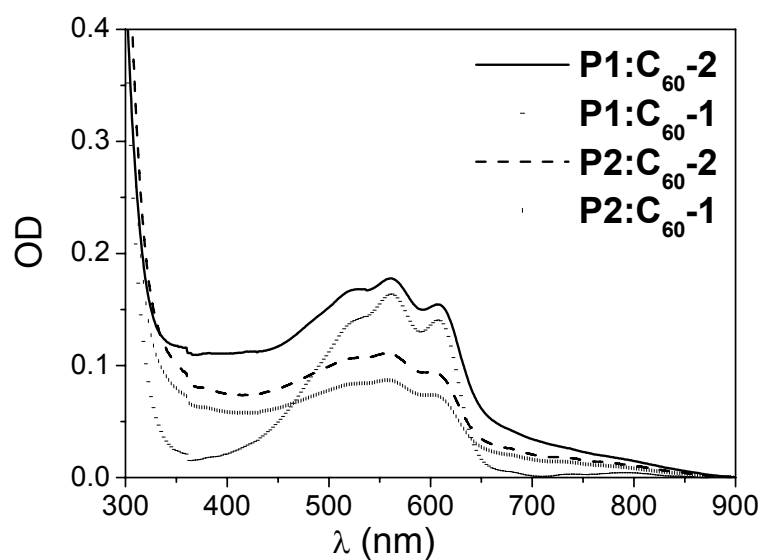


Figure S1 The UV-visible spectra of as-prepared film of pristine (top) and blend (bottom) films from o-DCB; films were spun on untreated glass substrates at 700 rpm for 60 s.

J-V curves

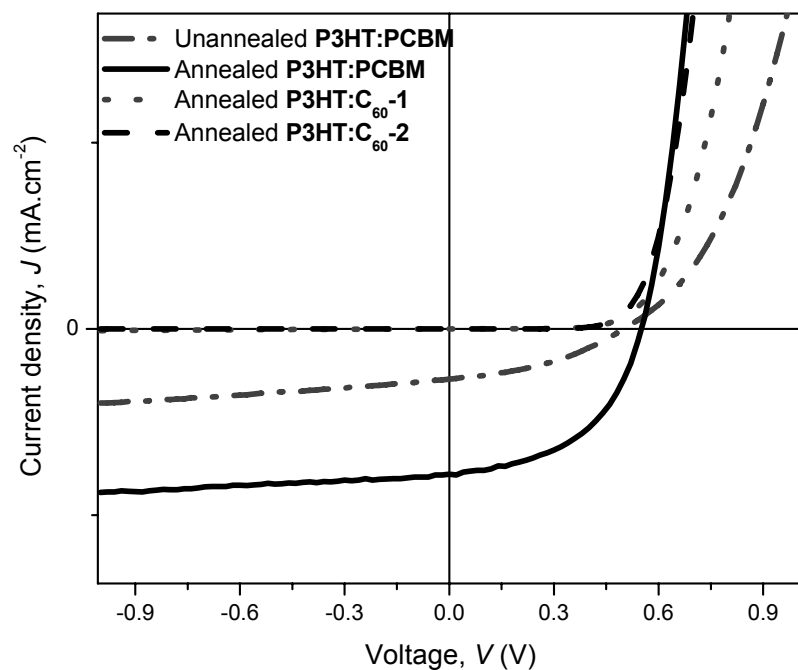


Figure S2 The J - V curves of P3HT:PCBM (solid and dotted black for annealed and non-annealed), P3HT:C₆₀-1 (red) and P3HT:C₆₀-2 (blue) photovoltaic device after annealing under constant illumination with 50 mW.cm⁻² AM1.5 simulated light at room temperature.

Reference

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